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PREPARATION AND STUDY OF SYNTHETIC PROTEIN-LIKE MATERIALS  
FOR HIGH PERFORMANCE ADHESIVE SYSTEMS

FINAL REPORT

CASE FILE  
COPY

Prepared by

Avco Systems Division  
Lowell Industrial Park  
Lowell, Massachusetts 01851

AVSD-0288-70-RR

Contract NAS 824074  
Control Number DCN 1-0-54-20029 (IF)

1 June 1970

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
GEORGE C. MARSHALL SPACE FLIGHT CENTER  
Huntsville, Alabama 35812

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W. S. Port  
B. W. Burrell

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# ABSTRACT

A program was undertaken to determine whether improved adhesive systems for aluminum 2014-T6 could be achieved by the use of primer coatings formulated from poly-L-Serine and poly-L-Tyrosine which have pendent polar groups (methylol and hydroxyphenyl, respectively) capable of quasi-chemical attachment to the substrate to be bonded and of chemical reaction with the resin used as the adhesive.

Specifically, the program comprised the following:

- a. treatment and characterization of the surface of aluminum alloy 2014-T6.
- b. evaluation of two methods for depositing the polymers on the substrate surfaces: deposition from solution and in situ polymerization.
- c. production of primer coatings by respective depositions from aqueous solution of poly-L-Serine and from dimethylformamide solution of poly-L-Tyrosine.
- d. lap shear testing of primed coupons bonded with an amine cured epoxy resin (Epon 828), and an anhydride cured epoxy resin (EpoxyLite 5403), respectively.

Three different primer thicknesses were evaluated by lap shear test for each polyamino acid with each epoxy adhesive. In EpoxyLite 5403 bonded systems, both primers decreased the lap shear strength by about 1000 psi. In the Epon 828 systems, poly-L-Serine brought about little or no improvement, but poly-L-Tyrosine (in thicknesses up to about one mil) increased the lap shear strength.

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## 1.0 INTRODUCTION AND SUMMARY

In the development of launch and space vehicles, new polymeric materials are needed as adhesive primers which maintain useful properties within the range 100° to 300° C.

Polymers which appear particularly promising are polypeptides having pendent polar groups which are capable both of quasi-chemical attachment to the substrate to be bonded and of chemical reaction with the resin system used as the adhesive. Synthetic poly-(amino acids) derived from L-Serine and L-Tyrosine, which have pendent methylol and hydroxyphenyl groups respectively, offer the possibility of hydrogen bonding to metal oxide surfaces (as, for example, to aluminum oxide) and of reacting with, for example, epoxy resin adhesive systems.

Accordingly, the primary objective of this program was to evaluate poly-L-Serine and poly-L-Tyrosine as primer coatings for aluminum alloy 2014-T6 bonded respectively with Epon 828, a bisphenol-A resin cured with diethylenetriamine and Epoxylite 5403, a modified, filled bisphenol-A resin cured with pyromellitic dianhydride.

The program consisted of three major tasks:

- a. aluminum surface preparation and characterization,
- b. primer coat formulation, deposition and characterization, and
- c. adhesive application and lap shear testing.

Task 1 comprised treating aluminum alloy coupons to produce two types of surfaces. In one type, chromic acid etching of the surface was followed by rinsing with a multivalent ion (i.e., sodium dichromate) (Refs. 1 and 2), solution to produce strongly adhering, but amorphous, non-hydrated aluminum oxide surface. In the other type, chromic acid treatment was followed by rinsing with deionized water at 60° C to produce a highly crystalline, but cohesively weak, tri-hydrated aluminum oxide surface, gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). The coatings formed under each rinse condition were characterized by electron microscopy techniques.

Task 2 comprised; a) evaluating two procedures for primer coat deposition, deposition from solution and in situ polymerization, b) developing film application techniques, and c) characterizing the films applied to freshly etched aluminum coupons. Deposition from solution for primer coat application was the method chosen after investigation showed that a linear, hydroxyl containing polymer could not be produced in situ on the aluminum oxide surface. Evaporation of aqueous solutions of poly-L-Serine or of dimethylformamide solutions of poly-L-Tyrosine were techniques which gave surfaces of controlled primer thicknesses. Characterization of the surfaces was achieved by infrared spectrophotometric analysis, x-ray diffraction, electron microscopy techniques, and metallographic examination. Metallographic examination was used to determine film thicknesses. Infrared analysis, x-ray diffraction, and electron microscopy were carried out to investigate the extent of bonding between polymer and aluminum. Infrared analysis indicated some bonding occurring between poly-L-Tyrosine and the aluminum oxide substrate. X-ray diffraction and electron microscopy could not detect this however.

An additional task consisted of investigating the thermal stability of poly-L-Serine and poly-L-Tyrosine by thermogravimetric analysis (TGA) and differential scan calorimetry (DSC).

Task 3 comprised the evaluation by lap shear tests of poly-L-Serine and poly-L-Tyrosine, respectively, as primer coatings for Epon 828 and Epoxylite 5403 adhesives.

## 2.0 RESULTS AND DISCUSSION

### 2.1 TASK 1 - ALUMINUM SURFACE PREPARATION AND CHARACTERIZATION

#### 2.1.1 Aluminum Surface Preparation

To obtain a strongly adhering, amorphous, non-hydrated aluminum oxide surface for optimum bonding, aluminum coupons were etched according to military specification MIL-A-9067C and rinsed by Wegman's "multivalent ion" procedure (Refs. 1 and 2). This procedure consisted of dipping the specimens five times in room temperature deionized water containing 150 parts per million of chromic oxide, as sodium dichromate, followed by dipping five times in room temperature deionized water. Wegman has found that multivalent compounds, including sodium dichromate, added to deionized rinse water prevent hydrate formation apparently by being preferentially absorbed into the surface to block the entrance of water. Hydrate formation is undesirable because a hydrated aluminum oxide coating is cohesively weak and causes bond failures at relatively low strengths.

To compare the surface produced by the "multivalent ion" rinse with that of a hydrated surface, a few specimens were rinsed for 10 minutes in 60° C deionized water. This procedure produced a tri-hydrated, highly crystalline aluminum oxide, gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ).

#### 2.1.2 Aluminum Surface Characterization

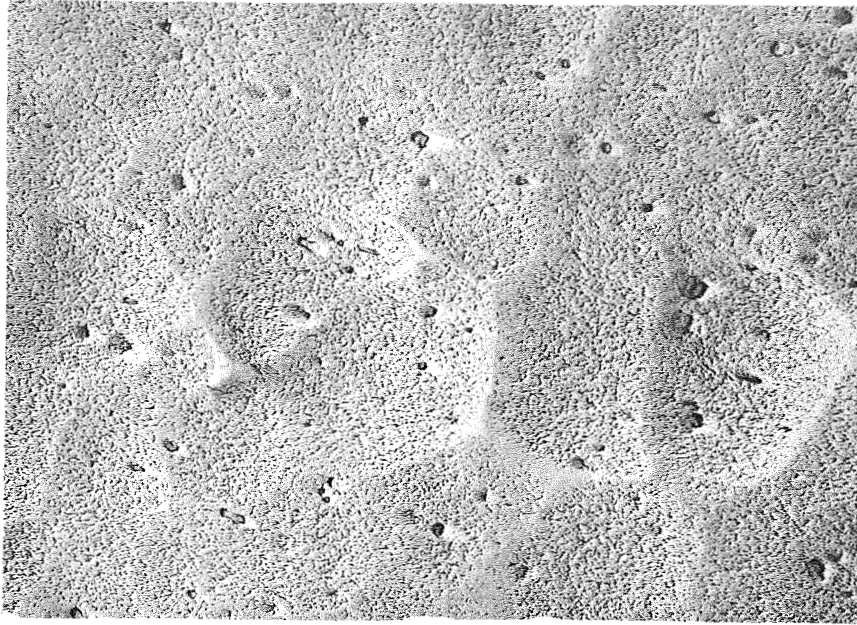
The treated coupons were examined by electron microscopy. The results are shown in Figures 1, 2, 3 and 4. Figure 1 is an electron micrograph of the anhydrous aluminum surface prepared by the "multivalent ion" rinse. Figure 2 shows the gibbsite surface. Figure 3 presents a reflection electron pattern for an un-etched aluminum surface and Figure 4 shows the diffraction pattern obtained for the gibbsite surface. No pattern could be obtained for the amorphous surface. A comparison of the amorphous and hydrated surfaces (Figures 1 and 2) shows that the amorphous surface does not have the cell base structure of the gibbsite. This is consistent with the lack of sealing of the aluminum surface by build-up of a hydrated aluminum oxide as noted by Wegman.

### 2.2 TASK 2 - PRIMER COAT FORMULATION, DEPOSITION AND CHARACTERIZATION

#### 2.2.1 Primer Coat Formulation and Deposition Studies

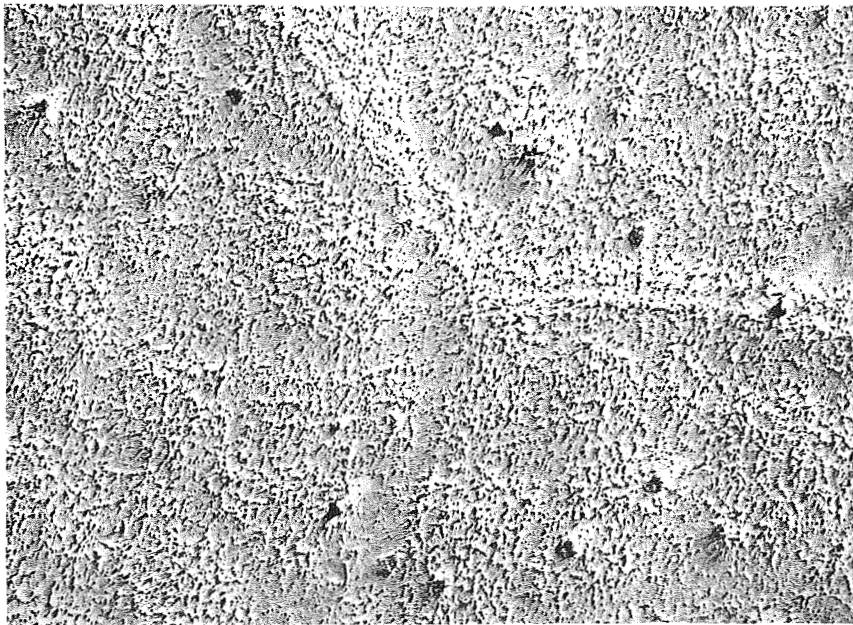
Polymer deposition from solution was the method selected to cast poly (amino acid) films on the aluminum oxide surfaces. The poly (amino acids) selected were required to have the capability of both bonding to the alumina surface by quasi-chemical means and to an epoxy adhesive by a chemical mode. Poly (amino acids) containing pendent hydroxyl groups, in particular poly-L-Serine and poly-L-Tyrosine, were selected as meeting this requirement.

The deposition method consisted of dissolving the polymer and evaporating the solution onto a freshly prepared aluminum alloy coupon. It was one of two methods selected for evaluation. The other method, a synthetic route to effect polymerization of N-Carboxyanhydrides to produce the poly (amino acids) in situ



69836

7500X



69834

15000X

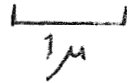
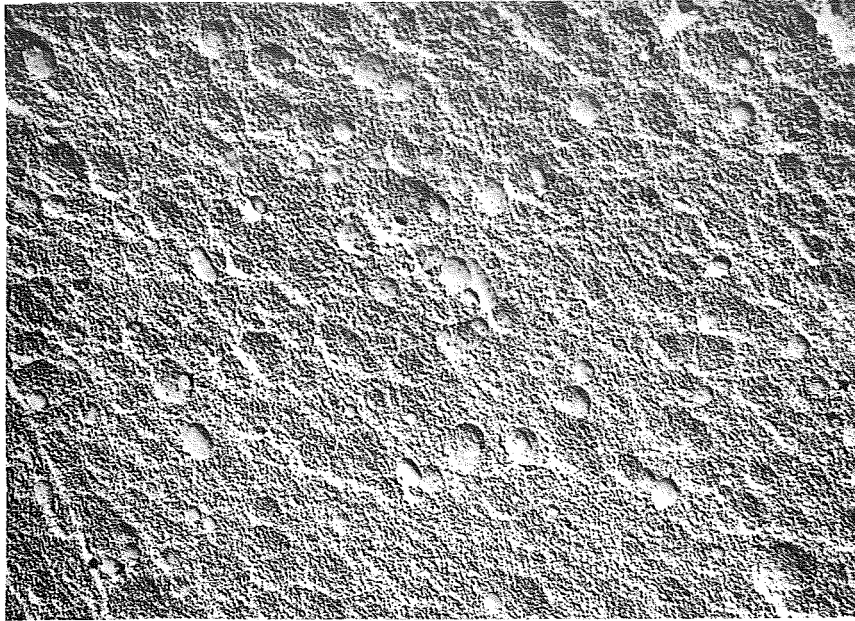
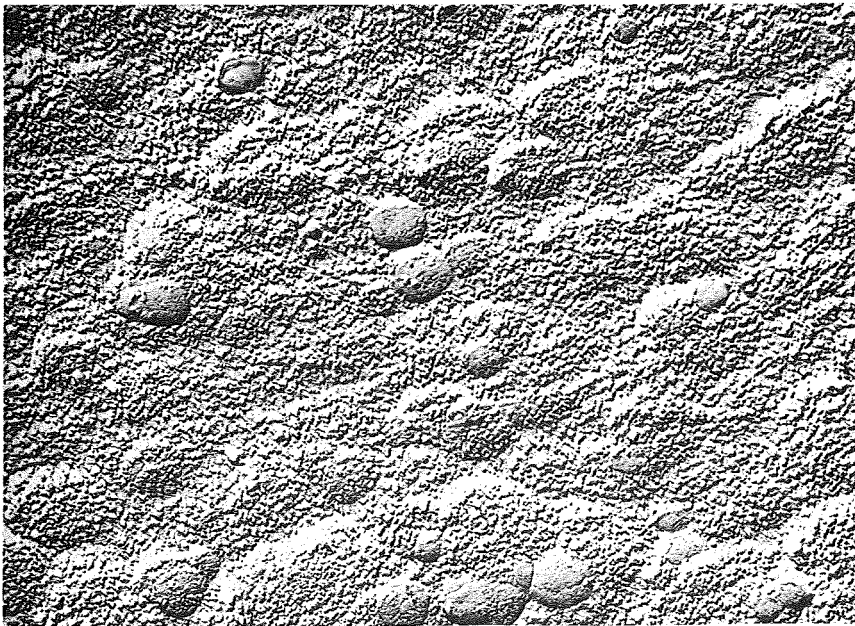


Figure 1 ELECTRON MICROGRAPH OF AMORPHOUS, NON-HYDRATED ALUMINUM  
SURFACE PREPARED BY CHROMIC ACID ETCH FOLLOWED BY  
"MULTIVALENT ION" RINSE



69734

7500X



69735

15000X

1.5mm=0.1  $\mu$   
or 1000 Å

Figure 2 ELECTRON MICROGRAPHS OF THE OXIDE SURFACE (GIBBSITE) FORMED  
BY CHROMIC ACID ETCH FOLLOWED BY 10 MINUTE RINSE IN 60° C  
DEIONIZED WATER

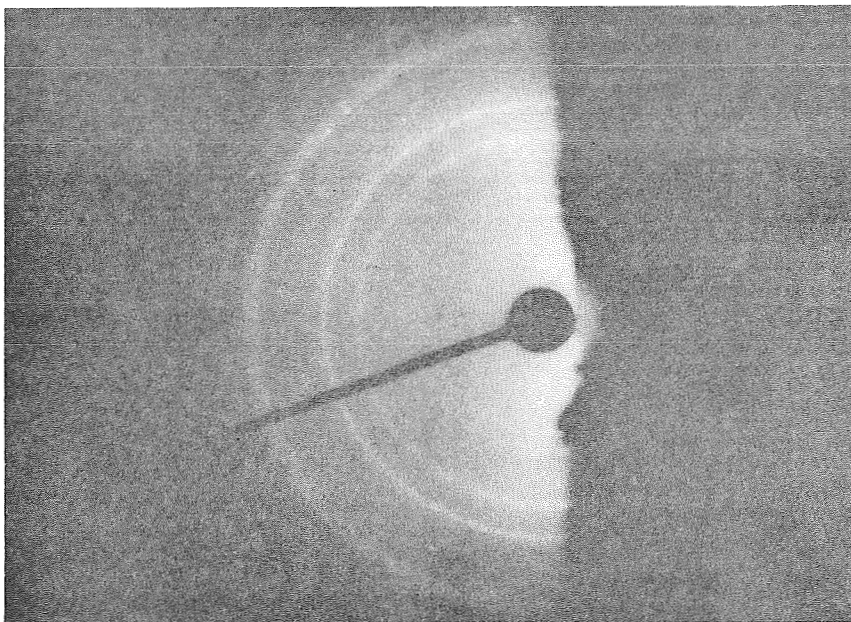


Figure 3 REFLECTION ELECTRON DIFFRACTION PATTERN OF UN-ETCHED ALUMINUM SURFACE

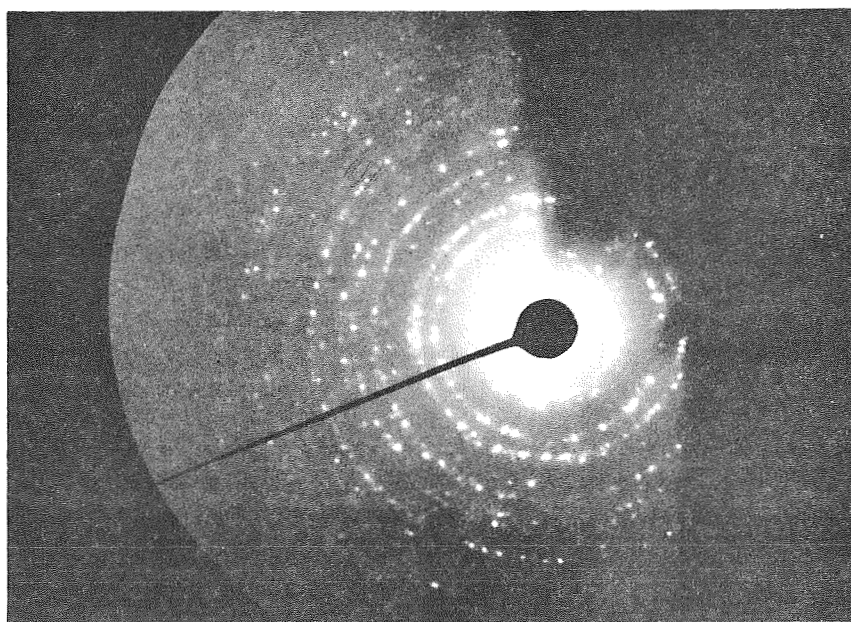
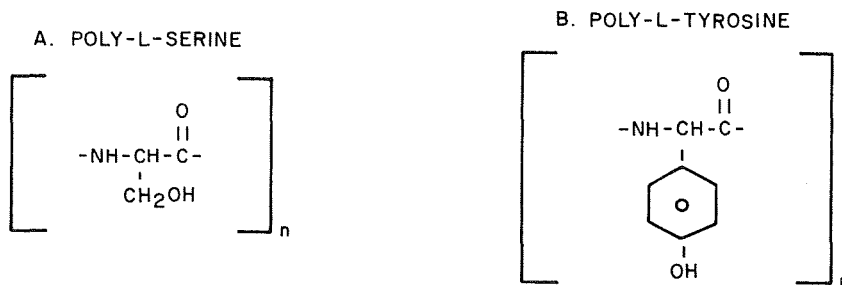


Figure 4 REFLECTION ELECTRON DIFFRACTION PATTERN OF ALUMINUM SURFACE (GIBBSITE) FORMED BY CHROMIC ACID ETCH FOLLOWED BY 10 MINUTE RINSE IN 60° C DEIONIZED WATER

on the metal oxide surface, was abandoned when it was found that a linear polymer cannot be prepared by polymerizing L-Serine-N-Carboxyanhydride.\*) Presumably all other hydroxy bearing N-carboxyanhydrides would also cross-link during polymerization.

Deposition from solution was carried out using poly-L-Serine and poly-L-Tyrosine purchased from Pilot Chemicals, Waltham, Massachusetts. Both polymers are linear, hydroxyl containing compounds. The poly-L-Serine used had a molecular weight of about 8000 which corresponded to a degree of polymerization (DP) of about 92. The molecular weight of the poly-L-Tyrosine used was about 100,000 which was equivalent to a DP of approximately 670. The formulas of these materials are:



Poly-L-Serine is soluble in water. Poly-L-Tyrosine is insoluble in water, alcohol, and pyridine, but was found to be soluble in dimethyl-formamide. (See Appendix B for details of the investigation into the solubility of poly-L-Tyrosine.)

To obtain uniform deposition of these polymers on prepared aluminum surfaces required some investigation into film forming techniques. The method found most satisfactory for producing films comprised evaporating a known volume of solution of known concentration from the aluminum surface by means of infrared heating lamps. (Water was used as the solvent for poly-L-Serine and dimethylformamide for poly-L-Tyrosine.) The solution was added dropwise onto the aluminum coupon and was spread and smoothed carefully to the edges with a rubber policeman as evaporation of the solvent proceeded. This was necessary because it was found that the solution had a tendency to retreat from the edges as the solvent was vaporized. To confine the solution to the desired area of the coupon (one-half square inch for lap shear test specimens), a barrier was constructed with a strip of pressure-sensitive cellophane tape or of aluminum foil held in place by the tape.

A multiple dipping method was also tried unsuccessfully during the first part of the program but the procedure was discarded when it was found that each dipping caused re-solution of the polymer film previously deposited.

## 2.2.2 Characterization of Primer Coat Films

### 2.2.2.1 Metallographic Examination

To evaluate the uniformity and thickness of the films deposited on the aluminum coupons, metallographic examination was employed. The coupons were cross-

\* Details of the attempted synthesis are presented in Appendix A.

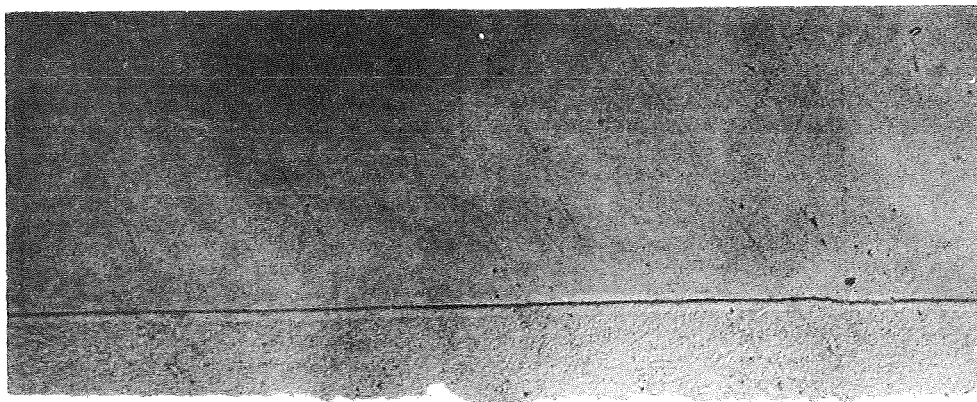
sectioned, mounted in an epoxy resin matrix, polished and viewed with a microscope. Figure 5 is a photograph of a 1.0 mil poly-L-Tyrosine film produced on an aluminum coupon by the technique described in paragraph 2.2.1. Figure 5 shows the film, aluminum substrate, and epoxy mounting matrix magnified 500 times. In the photograph, the aluminum substrate is at the bottom and labeled "c". The film, sandwiched between the upper epoxy matrix (labeled "a") and the aluminum, is labeled "b". It can be seen that the poly-L-Tyrosine adheres closely to the somewhat irregular surface of the aluminum, there being no obvious voids along the bond line. Additionally, there is apparent bonding between the film and epoxy resin matrix which is a bisphenol A-amine cured resin similar to the bonding agents used for lap shear testing in this program. (The results of lap shear tests, discussed in Section 2.3, confirm that some bonding or other interaction between poly-L-Tyrosine and the Epon 828 epoxy resin has occurred.)

It was found that films of poly-L-Serine could not be examined readily by metallographic techniques, because during the mounting and polishing process the film was damaged. Although efforts were made to avoid contact of the films with excessive amounts of moisture, it is believed that the presence of even small amounts of moisture in the polishing and mounting chemicals used caused film damage.

#### 2.2.2.2 Infrared Analysis

Films of poly-L-Serine and poly-L-Tyrosine deposited on etched aluminum coupons were analyzed by infrared (IR) spectroscopy to determine whether structural changes had occurred from bonding of the polymer with the aluminum substrate. Infrared spectra were obtained through the spectral region 4000 to 613  $\text{cm}^{-1}$  (2.5 to 16.3  $\mu$ ). The IR spectrum of a film of poly-L-Tyrosine on aluminum is shown as curve "a" in Figure 6. For comparison, a reference spectrum of a film cast on a potassium bromide window is shown as curve "b" in Figure 6.

The two spectra differ in that three bands, present in the reference spectrum (curve "b") at 1380, 720 and 650  $\text{cm}^{-1}$ , are missing in the spectrum of the film deposited on aluminum alloy 2014-T6 (curve "a"). It is conjectured on the basis of the following considerations that the absence of these bands indicates that part of the poly-L-Tyrosine molecule is chemisorbed on the aluminum oxide surface through hydrogen bonding, the hydrogens being contributed by both hydroxyphenyl and amide nitrogen groups. The band at 1380  $\text{cm}^{-1}$  in the reference spectrum, curve "b", is associated with oxygen-hydrogen deformation of the hydroxyphenyl structure. The disappearance of this absorption in the spectra of the film on the aluminum specimen suggests that such deformation can no longer occur because the hydrogen is bonded to the aluminum oxide surface. The bands at 720  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  in the reference spectrum are related to the secondary amide structure, and are termed Amide V and Amide IV, respectively. The Amide V band results from nitrogen-hydrogen deformation vibrations in hydrogen bonded secondary amides. The Amide IV band originates in structural skeletal mode vibrations. The absence of these absorptions in the spectrum of the aluminum deposited film suggests that hydrogen bonding also is taking place between amide hydrogens and the oxide surface coating.

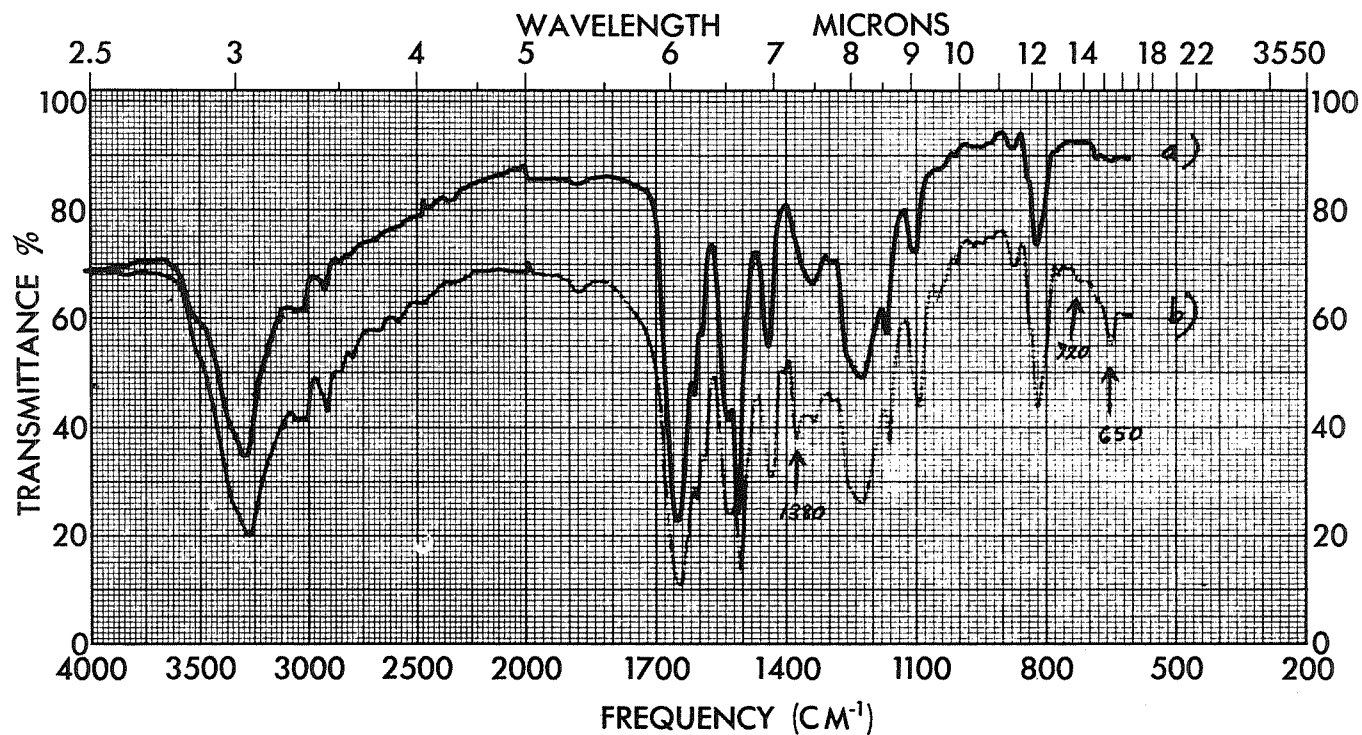


a

b

c

Figure 5 1.0 MIL POLY-L-TYROSINE FILM ON ALUMINUM



SPECTRUM NO. <u>6045</u>	ORIGIN <u>B. Burrell</u>	LEGEND _____	REMARKS _____
SAMPLE <u>Poly-L-Tyrosine</u>		1. _____	<u>a) on Al 2014-T6</u>
	PURITY _____	2. _____	<u>b) on salt chip</u>
	PHASE _____	DATE <u>1-15-70</u>	
	THICKNESS _____	OPERATOR <u>M. Brash</u>	

SPECTRUM NO. \_\_\_\_\_  
SAMPLE \_\_\_\_\_

Figure 6 INFRARED SPECTRUM OF POLY-L-TYROSINE FILM ON a) ETCHED 2014-T6 ALUMINUM ALLOY) b) SILVER CHLORIDE WINDOW

The IR spectrum of a poly-L-Serine film on aluminum is shown as curve "a" in Figure 7. A reference spectrum of a film cast on a silver chloride window is presented as curve "b". In contrast to results for poly-L-Tyrosine, a comparison of the spectra of poly-L-Serine films presented in Figure 7 shows no structural changes which can be related to hydrogen bonding of the polymer to the oxide surface.

#### 2.2.2.3 X-ray Diffraction

X-ray diffraction analysis was attempted on the poly-L-Serine and poly-L-Tyrosine films to ascertain whether evidence for bonding between the polymers and the aluminum substrate could be discerned through changes in diffraction patterns. The uncoated portions of the coupons were analyzed as controls. No appreciable changes in diffraction patterns could be observed between coated and uncoated aluminum specimens for either polymer. The lack of appreciable differences indicates that the polymer coatings are thin and amorphous.

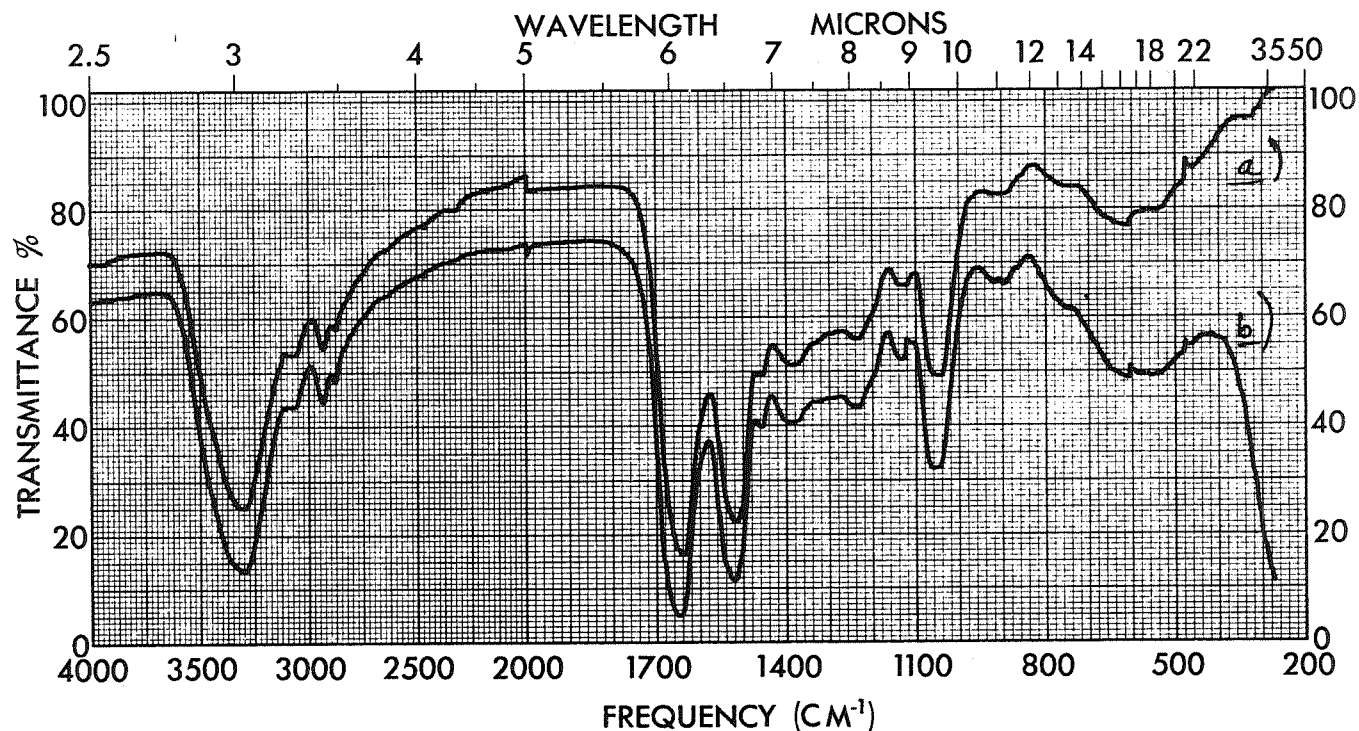
#### 2.2.2.4 Electron Microscopy and Electron Diffraction

The films were examined both by electron microscopy and electron diffraction. Although electron diffraction confirmed the x-ray diffraction finding and showed that the poly-L-Serine film was largely amorphous, evidence was found for a number of single crystals of the polymer coating. Figure 8 is a photomicrograph of a single crystal of poly-L-Serine on the surface of the aluminum. Figure 9 is the electron diffraction pattern obtained for this crystal.

Apparently, the poly-L-Serine coating consists largely of amorphous polymer in which some crystals are scattered. The film of poly-L-Tyrosine is non-crystalline, and displays a different microstructure than does poly-L-Serine. Figure 10 is a photomicrograph of the poly-L-Tyrosine film; its microstructure appears to comprise a series of ridges. Figure 11 is a photomicrograph of the poly-L-Serine film; its microstructure appears to comprise numerous spherical particles or globules. The different microstructure of the two polymers may be related to molecular structure. Amorphous polymers are composed either of chains coiled into globules or of packets of uncoiled or extended chains (Ref. 3). In this case, it appears that the poly-L-Serine, which has only a pendant hydroxy group and exists in a random configuration in the solid state (Ref. 4), has coiled into globules. Conversely, the poly-L-Tyrosine has a comparatively large, pendant hydroxyphenyl group which prevents the polymer from coiling into globules and forces it to form packets of extended chains.

#### 2.2.2.5 Ancillary Characterization of Primer Coat Polymers

As part of the characterization of poly-L-Serine and poly-L-Tyrosine, thermal stability information was obtained by thermogravimetric analysis (TGA) in air and helium and differential scan calorimetry (DSC) in nitrogen. Figures 12 and 13 show the weight lost with increasing temperature by 100 mg of poly-L-Serine heated in air and helium, respectively, from room temperature to 800° C at 10° C per minute. Figures 14 and 15 show results for 100 mg of poly-L-Tyrosine heated under the same conditions used for poly-L-Serine. Table I presents the percent total weight lost for each polymer in air and helium at 100° C temperature intervals.



SPECTRUM NO. <u>6053</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>Poly-L-Serine</u>	_____	1. _____	<u>Curve a = 2014-T6 Al alloy</u>
<u>Films cast from aqueous</u>	PURITY _____	2. _____	<u>Curve b = AgCl Window</u>
<u>solution</u>	PHASE _____	DATE <u>1-15-70</u>	_____
_____	THICKNESS _____	OPERATOR <u>BWB</u>	_____

SPECTRUM NO. \_\_\_\_\_  
SAMPLE \_\_\_\_\_

Figure 7 INFRARED SPECTRUM OF POLY-L-SERINE FILM ON  
a) ETCHED 2014-T6 ALUMINUM ALLOY  
b) SILVER CHLORIDE WINDOW

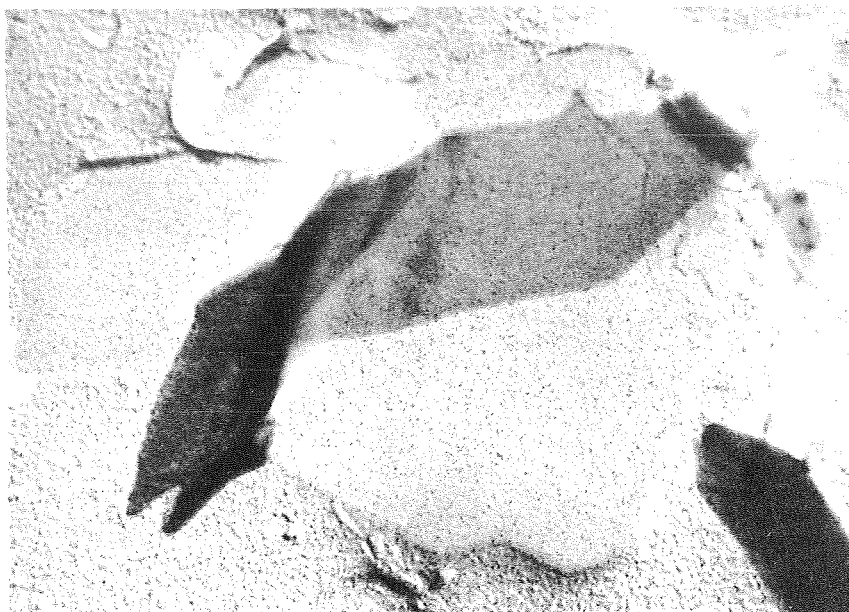


Figure 8 SINGLE CRYSTAL OF POLY-L-SERINE COATING ON ALUMINUM SURFACE

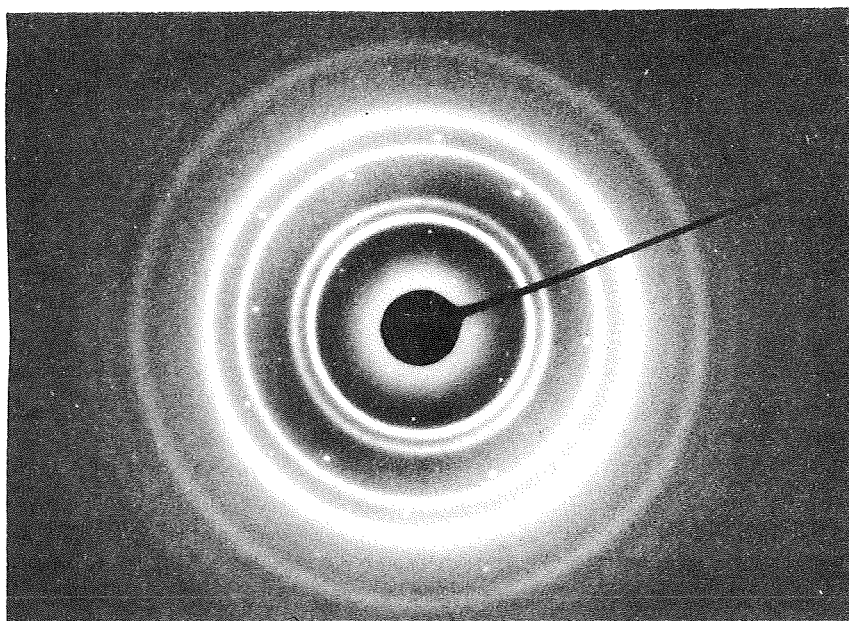


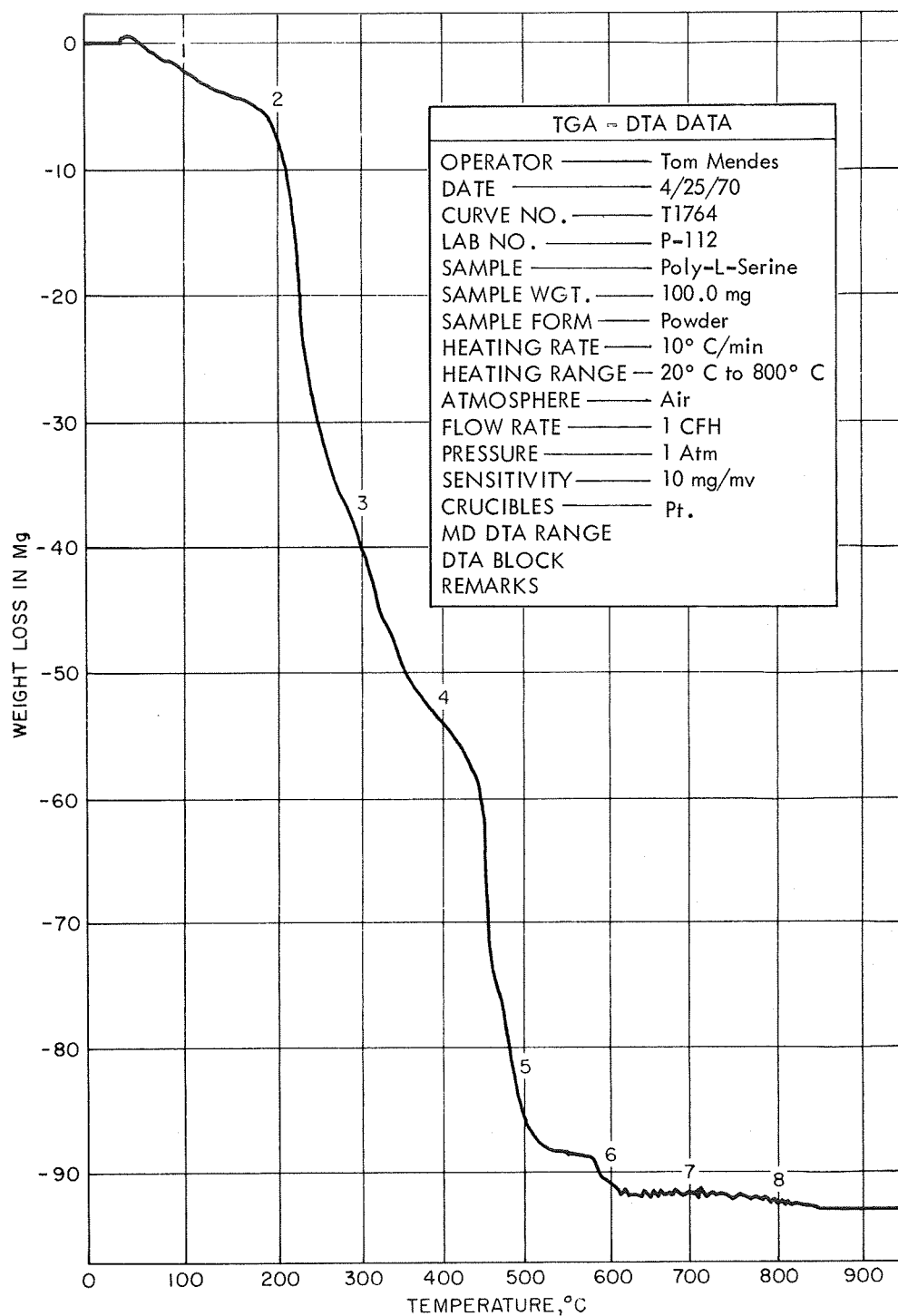
Figure 9 ELECTRON DIFFRACTION OF POLY-L-SERINE SINGLE CRYSTAL



Figure 10 ELECTRON MICROGRAPH OF SURFACE OF POLY-L-TYROSINE

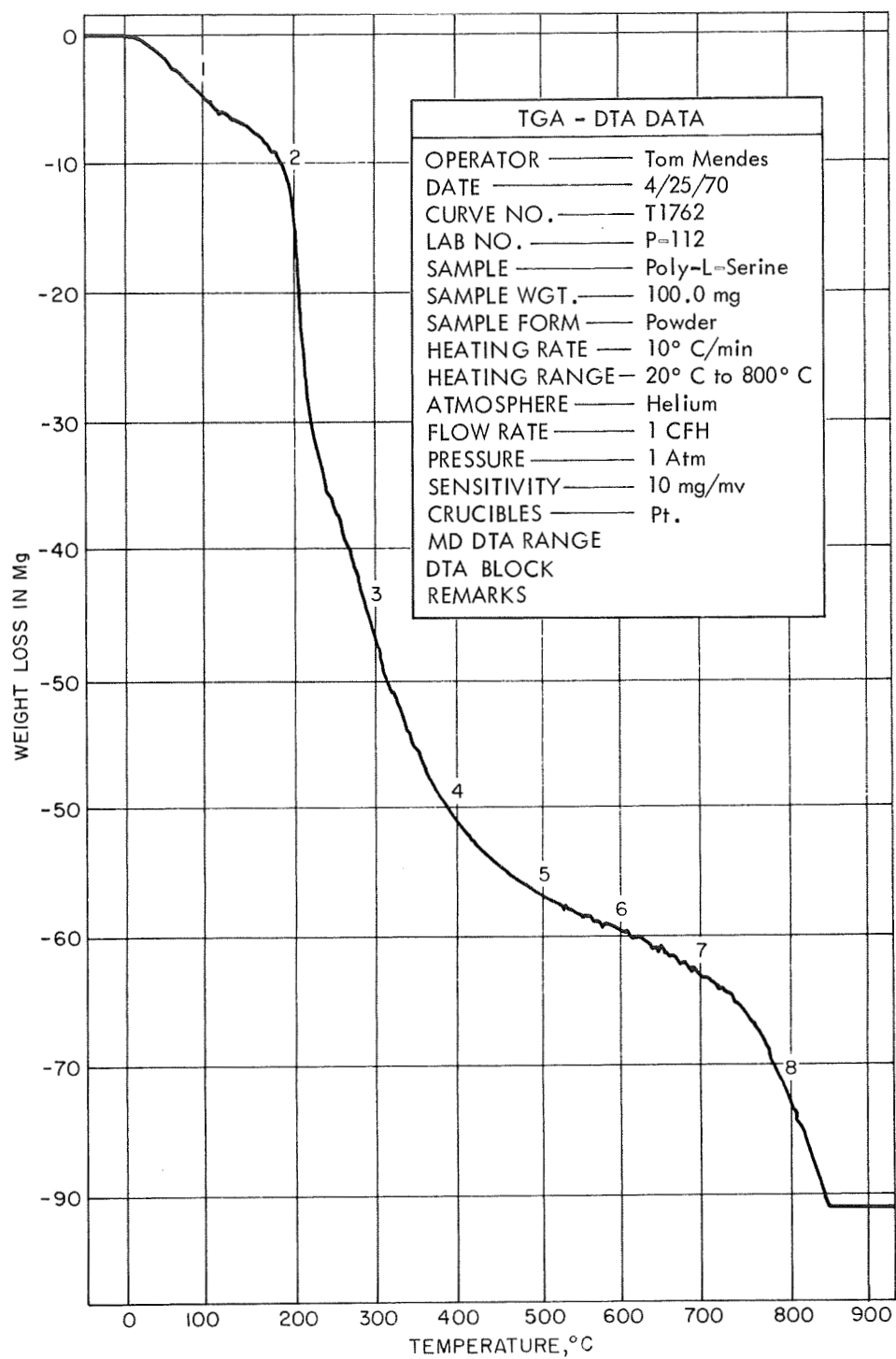


Figure 11 ELECTRON MICROGRAPH OF SURFACE OF POLY-L-SERINE



80-7965

Figure 12 THERMOGRAVIMETRIC ANALYSIS TRACE OF POLY-L-SERINE HEATED IN AIR FROM ROOM TEMPERATURE TO 800° C AT 10° C PER MINUTE



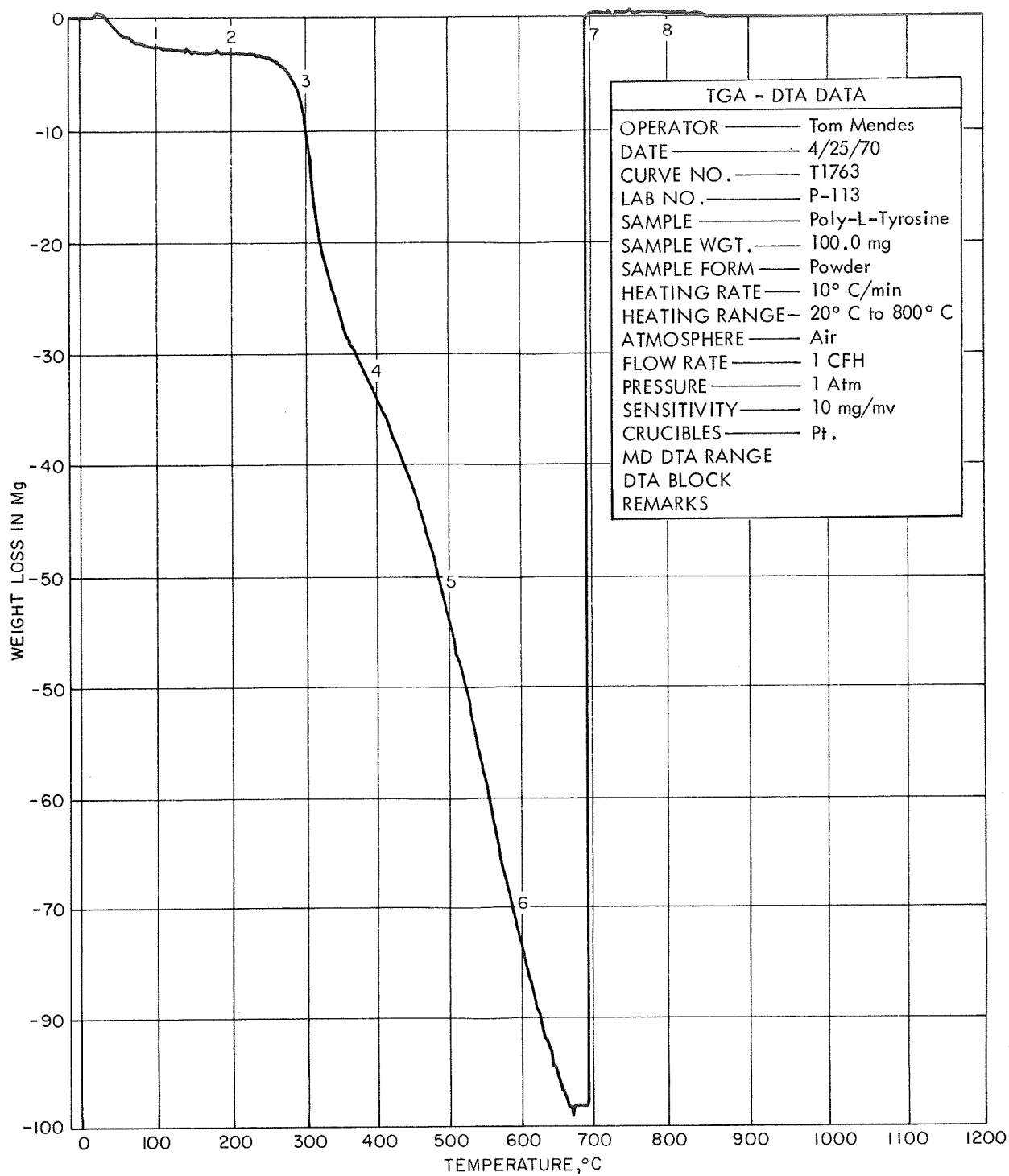


Figure 14 THERMOGRAVIMETRIC ANALYSIS TRACE OF POLY-L-TYROSINE HEATED IN AIR FROM ROOM TEMPERATURE TO 800° C AT 10° C PER MINUTE

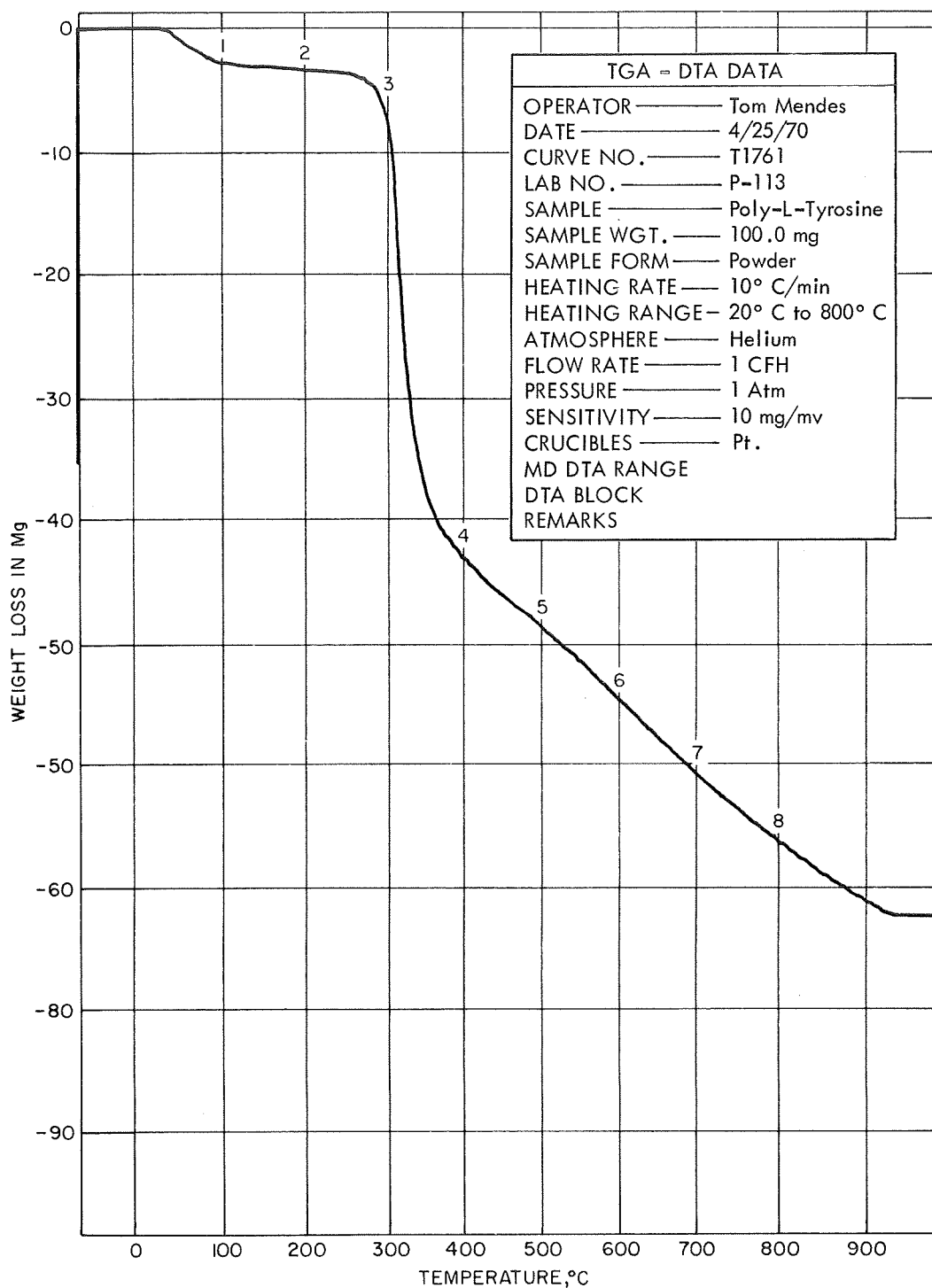


Figure 15 THERMOGRAVIMETRIC ANALYSIS TRACE OF POLY-L-TYROSINE HEATED IN HELIUM FROM ROOM TEMPERATURE TO 800° C AT 10° C PER MINUTE

TABLE I

THERMOGRAVIMETRIC DATA FOR POLY-L-SERINE AND POLY-L-TYROSINE  
IN AIR AND IN HELIUM; HEATING RATE = 10° C/MINUTE

Temperature °C	Total Weight Loss, percent			
	Air		Helium	
	Poly-L-Serine	Poly-L-Tyrosine	Poly-L-Serine	Poly-L-Tyrosine
100	2.0	2.9	4.5	2.5
200	7.0	3.0	11.0	3.5
300	40.0	10.0	47.0	7.0
400	54.5	34.0	61.0	43.0
500	86.5	54.5	67.0	49.0
600	91.5	84.0	69.5	54.7
700	92.0	100.0	73.0	61.0
800	92.5	100.0	83.0	66.5

The TGA results show that poly-L-Tyrosine is more stable in both air and helium than is poly-L-Serine which has lost significant weight, 11 and 7 percent respectively, in air and helium at 200° C. Poly-L-Tyrosine loses 3 to 3.5 percent in this temperature range. Also, poly-L-Serine begins degrading rapidly at 200° C whereas poly-L-Tyrosine does not begin degradation until about 280° C. These differences in degradation temperatures are attributable to both differences in molecular weight (8000 for poly-L-Serine and 100,000 for poly-L-Tyrosine) and the stabilizing phenyl ring constituent of the poly-L-Tyrosine. For both polymers, the rapid weight losses occurring below 400° C are probably caused by splitting out of carbon dioxide, water and ammonia. When this occurs, further cross-linking takes place and the new polymeric material degrades at a slower rate as heating is continued.

DSC was carried out by heating 5 mg of each polymer in nitrogen from room temperature to 540° C at a rate of 10° C per minute. The results could not be interpreted quantitatively because in each case a complex and erratic recorder tracing was obtained because of the polymer expanding out of the sample cup during heating. This effect was very much exaggerated in poly-L-Serine which intumesced to a great extent. However, the results were consistent with the TGA results and showed the following:

a. Poly-L-Serine

There was no apparent reaction from room temperature to 184° C. At 184° C there was a slight exothermic trend and at 207° C degradation proceeded exothermically throughout the duration of the test. An exothermic reaction is consistent with the intumescenting of the poly-L-Serine.

b. Poly-L-Tyrosine

There was no apparent reaction until a temperature of 284° C was obtained. Reactions then proceeded endothermically up to 375° C. (Between 284° and 344° C, approximately 33 calories were consumed per gram of polymer.) From 375° to 540° C, the highest temperature of the test, no reaction was observed.

### 2.3 TASK 3 - ADHESIVE APPLICATION AND LAP SHEAR TESTS

Lap shear test specimens were prepared with two types of epoxy adhesives:

a) Epon 828, a diglycidyl ether of bisphenol-A resin type, cured at room temperature with diethylenetriamine, and, b) Epoxylite 5403, a filled, modified bisphenol-A resin type cured at high temperature with pyromellitic dianhydride.

Test specimens were prepared from freshly etched 2014-T6 aluminum strips, 1 inch wide, 4 inches long, and 0.062 inch thick. Three groups of test specimens, each group containing six replicates, were prepared with each adhesive. One group remained unprimed to serve as a control, another group was primed with poly-L-Serine and the third primed with poly-L-Tyrosine. Primer was applied to one end of a strip over an area of slightly more than one-half of a square inch. Three different thicknesses of primer coat were evaluated. Specimens were so prepared as to give thicknesses on the order of 0.5, 1.0 and 1.5 mil. As a group of test specimens was primed, a sample coupon was prepared for metallographic examination to determine actual film thicknesses which are listed in Table II. Adhesive was applied over the primed area and covered a total area not greater than three quarters of a square inch. Strips were then aligned in a bonding fixture so that prepared ends overlapped one inch. Bond line thicknesses averaged approximately 5 mils. The specimens bonded with Epon 828 were set aside for one week to ensure full resin cure. The Epoxylite 5403 bonded specimens were cured for 16 hours at 210° F. After being cured, the specimens were tested in shear at 75° F according to the procedure of ASTM D1002-64 using a loading rate of 600 to 700 psi per minute.

TABLE II

#### PRIMER COAT THICKNESSES, MIL

Adhesive System Epon 828		Epoxylite 5403	
As Prepared	Measured	As Prepared	Measured
0.5	0.12	0.5	0.12
1.0	0.5	1.0	1.0
1.5	1.7	1.5	1.7

The lap shear test results are presented in Tables III, IV and V. The results show the following:

- a. In the Epoxylite 5403 systems, the controls failed cohesively, i.e., within the 5403 adhesive and not at the adhesive-aluminum surface interface. In the Epon 828 systems, however, the controls failed adhesively, i.e., at the adhesive-aluminum oxide interface. The differences in the type of bond failure and the failure load exhibited by these two resins are consistent with a greater bond strength existing between Epoxylite 5403 and the aluminum surface than between Epon 828 and the aluminum surface. Epon 828 is less flexible than Epoxylite 5403 and a lack of flexibility has been reported to decrease the interaction of the resin with the metal surface resulting in less adhesion (Ref. 5).
- b. In both the Epon 828 and Epoxylite 5403 systems, the primed coupons failed adhesively indicating relatively weak forces binding the poly-(amino acids) to the aluminum oxide.
- c. In the Epoxylite 5403 systems, both poly-(amino acid) primers caused decreases in failing loads (from the controls) amounting to greater than 1000 psi. However, poly-L-Tyrosine gave more consistent and higher failing loads than did poly-L-Serine. The decrease in failure loads for specimens primed with poly-L-Serine could have been caused in part by some deterioration of this polymer taking place during curing of the adhesive (16 hours at 210° F). However, poly-L-Tyrosine was shown to be stable at this temperature (100° C) and failure load values were nevertheless similar for primed specimens in both adhesive systems used. Therefore, the limiting factor is probably not the cure temperature but the inherently weak alumina-primer bond.
- d. In the Epon 828 systems, poly-L-Serine brought about little or no improvement in failing loads and exhibited, also, a wide variation in failing loads.
- e. Poly-L-Tyrosine significantly increased failing loads of the Epon 828 systems when present in film thicknesses of 0.12 and 0.5 mil (Tables III and IV) and decreased failing loads when present as a 1.7 mil coating (Table V). Table VI lists the differences between the mean failing loads of the Epon 828 controls and the poly-L-Tyrosine primed specimens for each of the film thicknesses evaluated. Figure 16 is a plot of this data which appears to have a linear relationship, and indicates that a poly-L-Tyrosine coating of less than about 1.3 mil will bring about an increase in mean failing load for Epon 828 bonded lap shear specimens under the test conditions used. The decrease in failure load (lap shear strength) with increasing thickness of the poly-L-Tyrosine is consistent with the results of other investigators (Ref. 6) and could be caused by the formation of large stresses in the poly-L-Tyrosine layer.

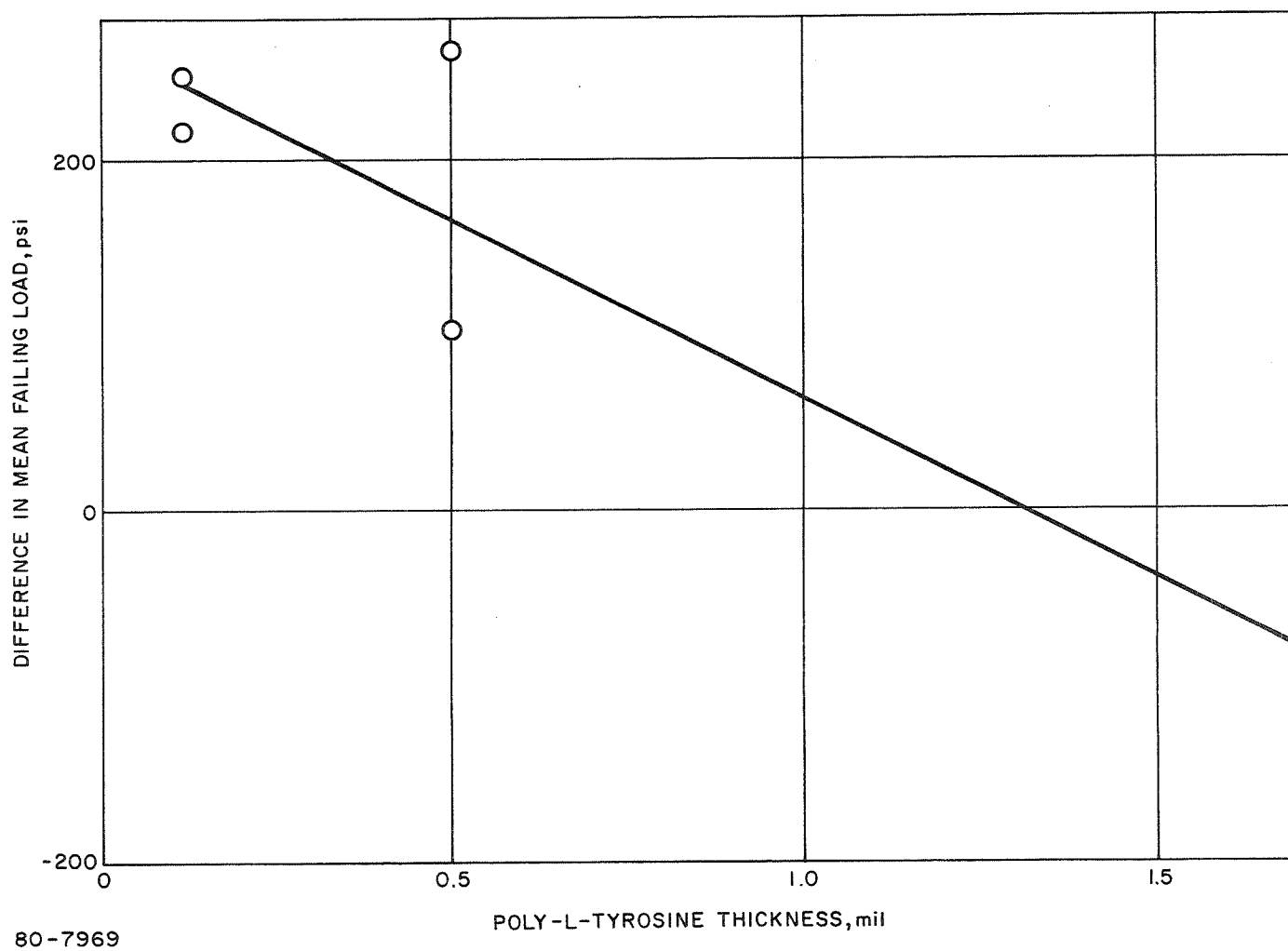


Figure 16 DIFFERENCE IN MEAN FAILING LOADS BETWEEN EPON 828 CONTROLS  
AND SPECIMENS PRIMED WITH POLY-L-TYROSINE VERSUS POLY-L-TYROSINE  
THICKNESS

TABLE III  
LAP SHEAR TEST RESULTS  
(MINIMUM PRIMER THICKNESS)

Primer Adhesive Trial	None				Poly-L-Serine				Poly-L-Tyrosine			
	Epon 828		EpoxyLite 5403		Epon 828		EpoxyLite 5403		Epon 828		EpoxyLite 5403	
	1	2	1	2	1	2	1	2	1	2	1	2
Primer Thickness, mil	---	---	---	---	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Failing Load, psi	796	744	2030	2200	422	584	630	225	880	912	320	1280
	714	722	1680	2490	688	1060	820	264	1004	1110	370	1290
	594	834	1640	2050	782	832	280	504	948	966	420	725
	656	866	2200	2260	1000	870	230	232	856	1120	380	785
	748	826	2000	1840	586	580	250	340	840	930	460	790
	626	854	2530	2160	806	664	250	296	--- <sup>b</sup>	1290	450	1510
Range	594-796	722-866	1640-2530	1840-2490	422-1000	580-1060	230-820	225-504	840-1004	912-1290	320-460	725-1510
Mean, $\bar{x}$	689	808	2013	2167	706	765	410	310	906	1055	400	1063
Av. Dev. from Mean	±64	±50	±240	±150	±157	±156	±210	±77	±56	±119	±43	±297
% Av. Dev. from Mean	9.2	6.2	12	6.9	22	20	51	25	6.2	11	11	28
Standard Deviation, $\sigma$	77	60	332	217	206	190	252	104	69	146	53	336
Type of Failure <sup>a</sup>	A	A	C	C	A	A	A	A	A	A	A	A

<sup>a</sup> A = adhesive, i.e., failure at the aluminum oxide - primer (or adhesive) interface.

C = cohesive, i.e., failure within the epoxy adhesive.

<sup>b</sup> Test was void.

TABLE IV  
LAP SHEAR TEST RESULTS  
(INTERMEDIATE PRIMER THICKNESS)

Primer Adhesive Trial	None				Poly-L-Serine				Poly-L-Tyrosine			
	Epon 828		EpoxyLite 5403		Epon 828		EpoxyLite 5403		Epon 828		EpoxyLite 5403	
	1	2	1	2	1	2	1	2	1	2	1	2
Primer Thickness, mil	---	---	---	---	0.5	0.5	1.0	1.0	0.5	0.5	1.0	1.0
Failing Load, psi	650	1120	1800	1970	1120	630	430	700	840	940	580	1030
	720	800	2140	2030	640	920	820	500	1230	970	580	830
	590	680	2090	1940	890	730	1680	490	900	1160	830	750
	615	670	2000	1970	430	1070	230	320	800	830	980	850
	630	950	1900	2130	875	780	300	800	930	740	780	1020
	815	830	2000	1790	700	800	230	520	920	1030	780	830
Range	590-815	670-1120	1800-2140	1790-2130	430-1120	630-1070	230-1680	320-800	800-1230	740-1030	580-980	750-1030
Mean, $\bar{x}$	670	842	1988	1972	776	822	615	555	937	945	755	885
Av. Dev. from Mean	±65	±129	±92	±72	±186	±116	±392	±130	±98	±108	±117	±93
% Av. Dev. from Mean	9.7	15	4.6	3.7	24	14	64	23	10	12	15	11
Standard Deviation, $\sigma$	84	171	124	112	239	154	559	170	152	148	49	114
Type of Failure <sup>a</sup>	A	A	C	C	A	A	A	A	A	A	A	A

<sup>a</sup>A = adhesive - failure at the aluminum oxide-primer (or adhesive) interface.  
C = cohesive - failure within the epoxy adhesive.

TABLE V  
LAP SHEAR TEST RESULTS  
(MAXIMUM PRIMER THICKNESS)

Primer Adhesive Trial	None				Poly-L-Serine				Poly-L-Tyrosine			
	Epon 828		Epoxylite 5403		Epon 828		Epoxylite 5403		Epon 828		Epoxylite 5403	
	1	2	1	2	1	2	1	2	1	2	1	2
Primer Thickness, mil	---	---	---	---	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Failing Load, psi	870	940	2140	2270	510	930	1430	1180	810	960	800	1480
	1230	810	2230	2150	1170	880	1400	1080	970	840	970	1070
	920	1080	2280	2300	780	880	820	580	1030	900	860	1080
	1230	1430	2100	2270	670	820	430	1570	880	980	700	1120
	1330	1060	1930	2180	1170	970	600	1430	1060	1220	1020	1180
	710	1060	1760	1690	870	600	1370	1530	1110	860	820	1250
Range	710-1330	810-1430	1760-2280	1690-2270	510-1170	600-970	430-1430	580-1570	810-1110	840-1220	700-1020	1070-1480
Mean, $\bar{x}$	1048	1063	2073	2143	862	847	1008	1228	977	960	862	1197
Av. Dev. from Mean	±215	±128	±152	±151	±210	±91	±392	±282	±90	±93	±89	±112
% Av. Dev. from Mean	21	12	7.3	7.1	24	11	39	23	9.2	9.7	10	9.4
Standard Deviation, $\sigma$	248	207	196	230	270	131	447	372	114	139	117	154
Type of Failure <sup>a</sup>	A	A	C	C	A	A	A	A	A	A	A	A

<sup>a</sup> A = adhesive, i.e., failure at the aluminum oxide-primer (or adhesive) interface.  
C = cohesive, i.e., failure within the epoxy adhesive.

TABLE VI

THE MEAN FAILING LOAD DIFFERENCES  
BETWEEN EPON 828 CONTROL AND  
POLY-L-TYROSINE PRIMED COUPONS

Poly-L-Tyrosine Film Thickness, mils	Mean Lap Shear Failing Load Differences	
	Trial 1	Trial 2
0.12	+ 217	+ 247
0.5	+ 267	+ 103
1.7	- 71	- 103

f. In both adhesive systems, poly-L-Tyrosine appears to bond consistently better with the aluminum oxide surface than does poly-L-Serine, although in both cases these bonds are weak when compared to those formed by Epoxylite 5403. One possible contribution to the weakness of the bond strength of the poly-(amino acids) to alumina arises from their deposition from dilute solution. Such deposition has been said to permit only a fraction of the active groups of the polymer chain to become anchored to the oxygenated metal substrate (Ref. 5).

The better performance of poly-L-Tyrosine may result from the presence of the hydroxyphenyl group which provides a greater area of polarity than does the methylol group of the poly-L-Serine and would tend to bond more strongly to the aluminum surface. Also, the insolubility in water of the poly-L-Tyrosine tends to decrease the extent of moisture solvation and hence of bond degradation. Finally, the possibility of plasticization of the normally brittle Epon 828 adhesive enabling it to withstand somewhat higher shear forces can not be excluded.

### 3.0 CONCLUSIONS

The following conclusions can be made from the results obtained in this program.

- a. Deposition from solution of poly-L-Serine or poly-L-Tyrosine is a suitable method for preparing primer coats on a prepared metal surface.
- b. In situ polymerization on the aluminum oxide surfaces of the N-Carboxyanhydrides of L-Serine or L-Tyrosine from solution does not appear feasible because cross-linking occurs and template conformance to the surface cannot be achieved.
- c. When used as primer coats for a high temperature anhydride cured resin system such as Epoxylite 5403, both poly-L-Serine and poly-L-Tyrosine decrease the lap shear strength of the adhesive.
- d. Under the lap shear test conditions used in this program, poly-L-Tyrosine used as a primer coat in thicknesses of up to about 1.3 mil will increase failure loads (compared with a control lacking a primer) for specimens bonded with Epon 828 adhesive cured at room temperature with diethylenetriamine. Conversely, the use of poly-L-Serine as a primer coat does not increase the failure load.
- e. The greater lap shear strength produced by poly-L-Tyrosine as a primer for the Epon 828 adhesive system may be ascribed to a stronger bonding of the poly-amino acid to the aluminum oxide surface than is formed by the resin alone. However, the possibility cannot be excluded that the poly-L-Tyrosine has a plasticizing effect on the normally brittle Epon 828 enabling it to withstand higher shear loads.

#### 4.0 RECOMMENDATIONS

Improved protein-like polymers for use as primer coatings in bonding oxygenated metal surfaces should comprise amino acid residues selected to impart the following properties to the macromolecule: conformance to the metal oxide surface, reactive (polar) groups, flexibility, insolubility in water, acids and bases, ability to form strong bonds with the adhesive to be used, and cohesive strength through a high molecular weight. It is envisioned that such macromolecules could be made by first linking perhaps 10 or more amino acids selected to impart the desired properties. The carboxy end group of the resulting low molecular weight amino acid oligomer would then be converted to a reactive polymerizable group, such as a glycidyl ester which can be polymerized together with a bis-phenol A type of resin. This resulting polymer would be of high molecular weight and contain poly-(amino acid) side groups designed to conform as much as possible to the metal substrate. The synthesis of the amino acids (oligomers) could be carried out by the solid phase method discovered by Merrifield (Ref. 7).

Conformance of the poly-(amino acids) to the metal substrate could be evaluated by infrared analysis while the evaluation of the bond strengths could be done by lap shear testing.

## 5.0 REFERENCES

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4. Fasman, G. D. and E. R. Blout, "The Synthesis and the Conformation of Poly-L-Serine and Poly-O-Acetyl-L-Serine," J. Am. Chem. Soc. 82, pp. 2262-2267 (1960).
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APPENDIX A

IN-SITU POLYMERIZATION PROCEDURES

## APPENDIX A

### IN-SITU POLYMERIZATION PROCEDURES

The in situ polymerization work consisted of two parts. The first was the deposition of the tertiary amine polymerization initiating agent on the prepared metal surface. The second was the attempted synthesis of the poly-L-Serine N-Carboxyanhydride (L-Serine NCA).

#### a. Amine Deposition

Two types of aluminum specimens were used; one type had a gibbsite surface coating, and the other had been treated with a multivalent ion rinse. A 0.1M solution of purified tripropylamine in cyclohexane was prepared. The two specimens were immersed in the solution and the solvent was removed by air drying. These specimens were examined by an infrared method and by electron microscopy. The infrared method consisted of heating the specimens in vacuo in a gas sampling cell and obtaining the infrared spectrum of the amine vapors. Electron micrographs (Figures A-1 and A-2) showed, also, that the surfaces had been coated with amine. Figure A-1 shows the surface of the multivalent ion rinsed aluminum before and after amine deposition, Figure A-2 shows the gibbsite coated aluminum sample which appears to have absorbed more amine than the non-hydrated surface.

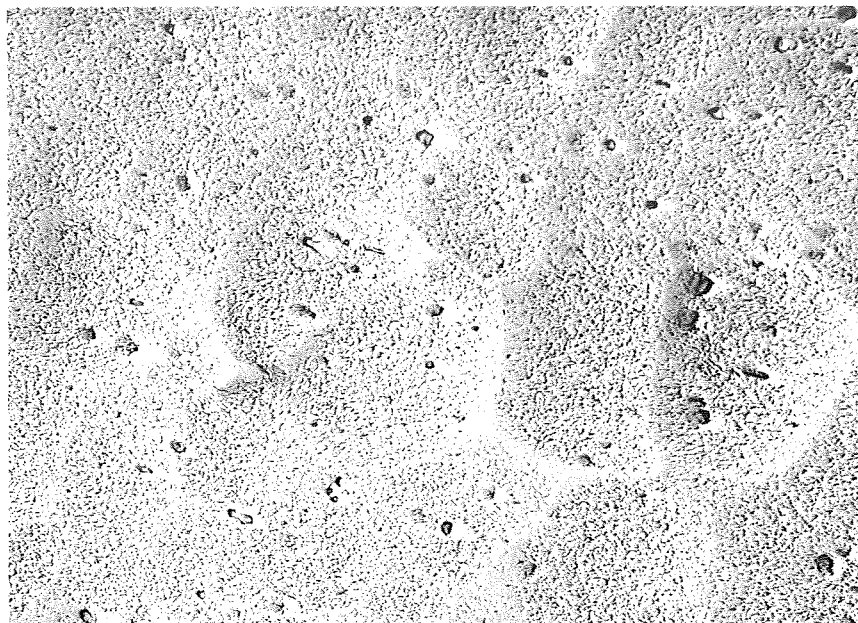
#### b. Poly-L-Serine Precursor Synthesis

Prior to beginning the preparation of the poly-L-Serine precursor, L-Serine-N-carboxyanhydride, Dr. E. Blout, Harvard Medical School, was consulted by telephone and he verified that poly-L-Serine can be obtained from the polymerization of L-Serine NCA in which the hydroxyl group was not blocked. Professor Blout had indicated in Ref. 4 that such polymerization was possible and would be reported subsequently, but had made no further publication of his later work.

Work was begun on the preparation of L-Serine-N-Carboxyanhydride (NCA) using the procedure outlined by Fasman and Blout (Ref. 4) in which the amino acid, suspended in dry ethyl acetate, is converted to the NCA by reaction with phosgene.

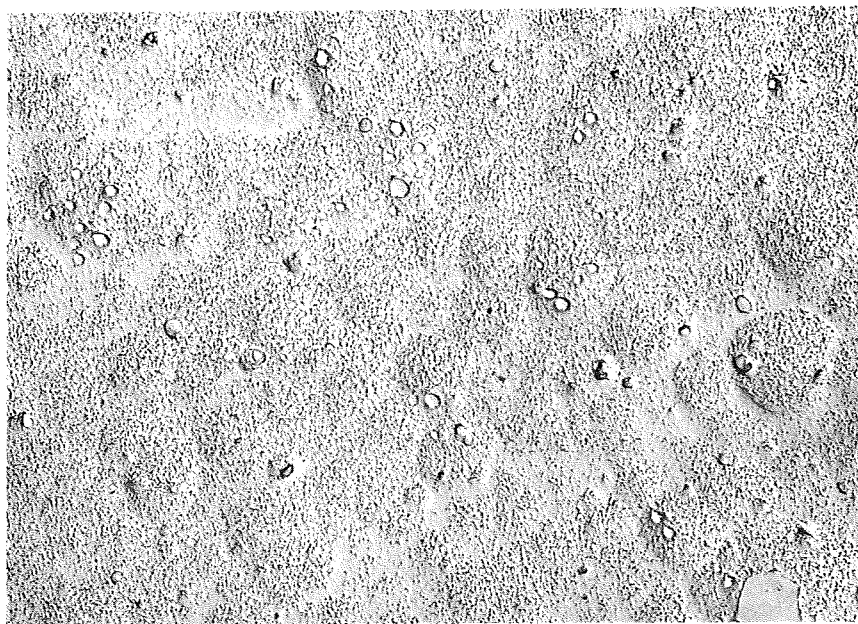
Four attempts to make the NCA were carried out. The first indicated that modifications to the apparatus were necessary in order to lessen the possibility of moisture introduction during vacuum distillation and solvent addition steps. The second preparation was carried out in the modified apparatus. The reaction proceeded smoothly during phosgene addition. After excess solvent had been removed by vacuum distillation, however, a white precipitate was obtained rather than the expected oil. Nevertheless, the experiment was carried to completion because of the possibility that the white precipitate was crystallized NCA. The eventual failure of this material to re-dissolve in additional solvent made it evident that the precipitated material was not the NCA.

To determine the identity of the product, its infrared spectrum was obtained. For comparison, an infrared spectrum of the starting amino acid, L-Serine was obtained. The spectra of both product and L-Serine are presented in Figures A-3



69836  
(a)

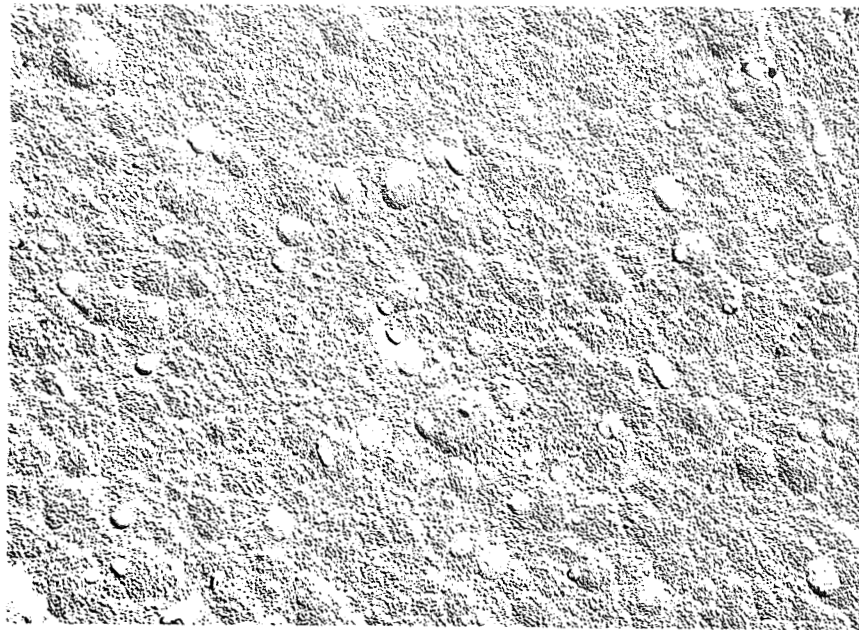
7500X



69909  
(b)

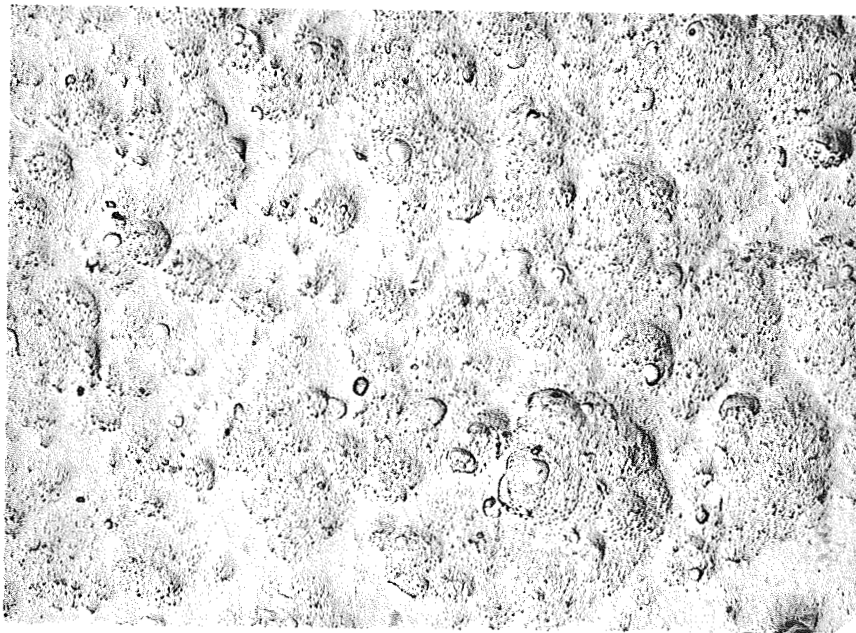
7500X

Figure A-1 ELECTRON MICROGRAPHS OF ALUMINUM SURFACES  
a) Non-hydrated Amorphous  $\text{Al}_2\text{O}_3$ ,  
b) Same Surface after Amine Treatment



69735  
(a)

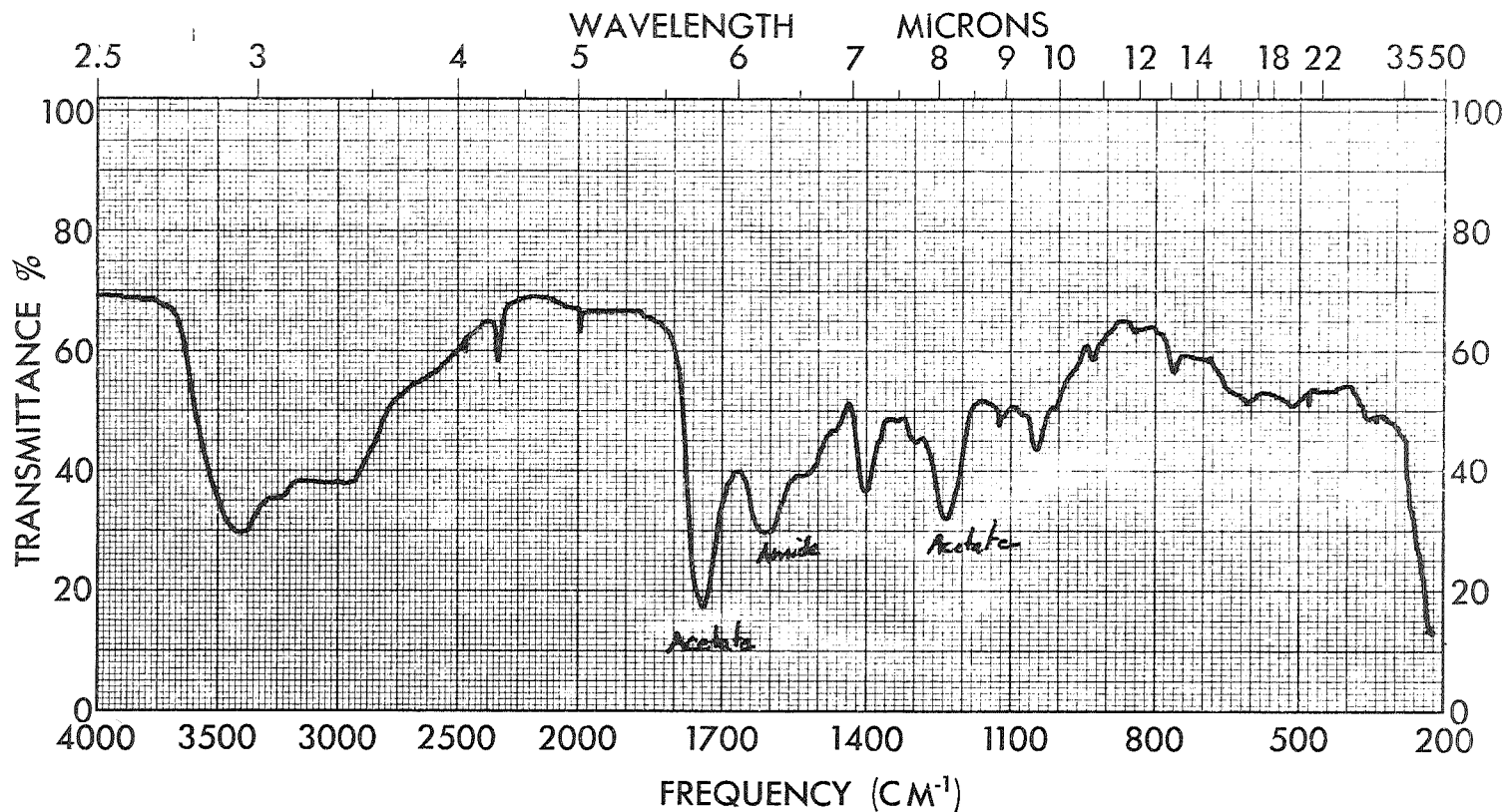
7500X



6991  
(b)

7500X

Figure A-2 ELECTRON MICROGRAPHS OF ALUMINUM SURFACES  
a) Gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ),  
b) Same Surface after Amine Coating



SPECTRUM NO. <u>5968</u>	ORIGIN <u>B. BURRELL</u>	LEGEND	REMARKS <u>Material is</u>
SAMPLE <u>N964</u>		1.	<u>Poly-L-Serine Contaminated</u>
<u>SYNTHETIC PRODUCT</u>	PURITY <u>1 MG</u>	2.	<u>with Ethyl Acetate.</u>
<u>OF L-SERINE AND</u>	PHASE <u>PELLET, KBr</u>	DATE <u>11-19-69</u>	
<u>COCl<sub>2</sub></u>	THICKNESS	OPERATOR <u>W. LADROGA</u>	

SPECTRUM NO. 5968  
SAMPLE N964

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION

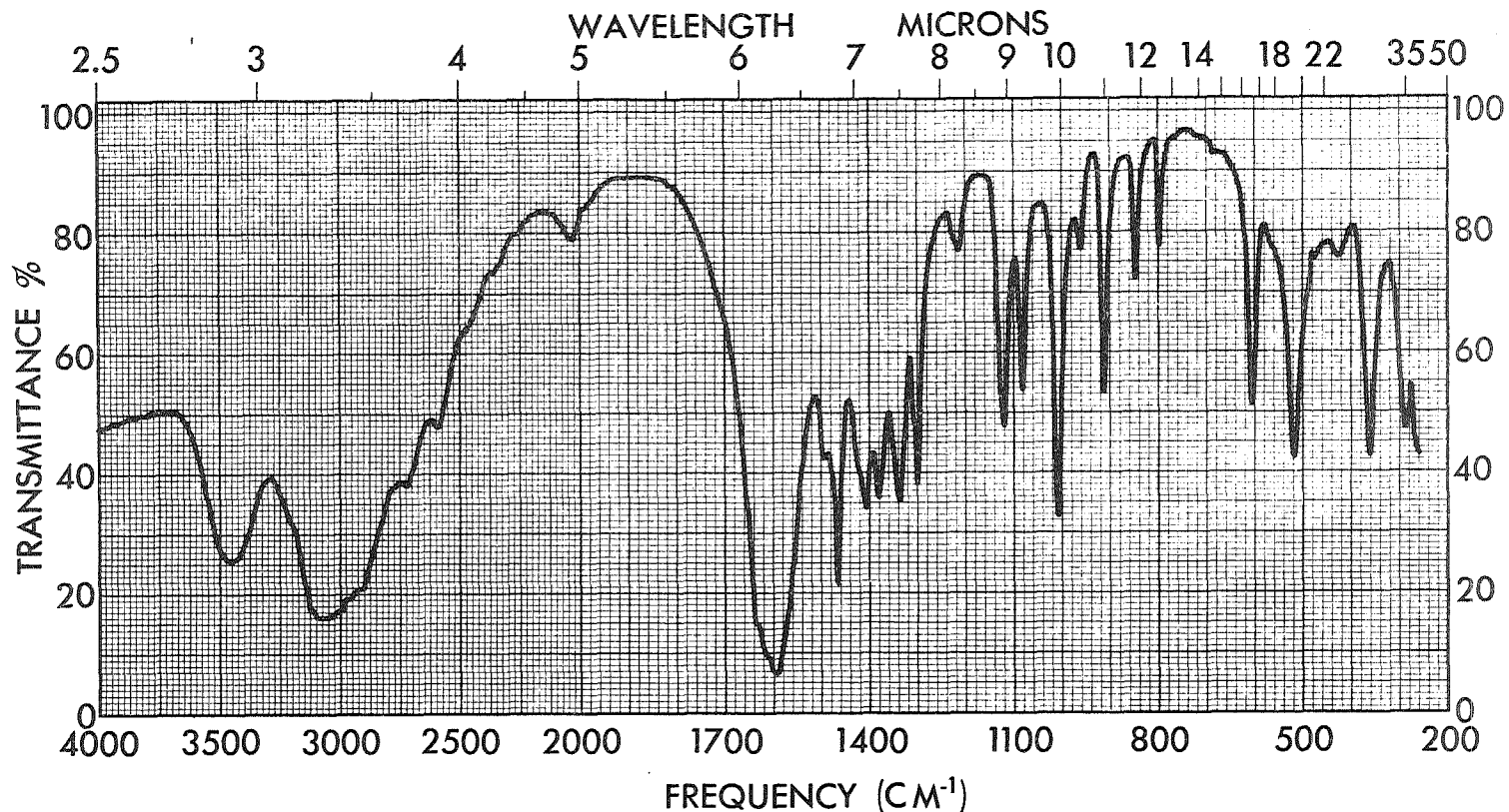
NORWALK, CONN.

Figure A-3 INFRARED SPECTRUM OF SYNTHETIC PRODUCT OF L-SERINE AND PHOSGENE

and A-4, respectively. Comparison of the product spectrum with other reference spectra and the information of Fasman and Blout (Ref. 4) show that the spectrum is that of polymerized L-Serine contaminated with ethyl acetate.

The formation of poly-L-Serine was consistent with the premature polymerization of L-Serine NCA during the removal of excess solvent by vacuum distillation. This was consistent with contamination of the reaction mixture with water vapor. For this reason, steps were taken to exclude, rigorously, the possibility of moisture contamination during the third preparation. Again, the expected product was not obtained. However, moisture was not a factor.

Apparently, the NCA had reacted while the solvent was being purged of phosgene by overnight refluxing. It was decided to carry out another reaction under exactly the same conditions except that the reaction flask would be allowed to cool to room temperature after completion of phosgene addition (about 3 hours). The system was purged overnight with dry nitrogen to remove excess phosgene. A white insoluble solid in the flask indicated that reaction had occurred to a much lesser extent than anticipated. Infrared spectroscopy showed that the solid was for the most part the starting amino acid, L-Serine. It was concluded from these trials that a good yield of L-Serine NCA could be expected only under rigidly controlled reaction conditions. To determine the exact procedure necessary for the preparation, M. Hyman, President of the Pilot Chemical Company of Waltham, Mass. was called. His company specializes in the manufacture of NCA and polyamino acids. Mr. Hyman's chemists were not acquainted with this particular preparation because the usual route to poly-L-Serine is through the O-acetyl-L-Serine NCA in which the hydroxyl group is blocked. It was learned from Mr. Hyman, however, that Dr. Fasman, who with Dr. Blout, published the synthesis of L-Serine NCA (Ref. 4), is presently at Brandeis University. Dr. Fasman was consulted concerning our difficulties and concurred with our conclusions that a good yield of L-Serine NCA would probably result if reflux were continued after phosgene addition only until most of the suspended L-Serine had dissolved. However, it was also learned from Dr. Fasman, coauthor of the cited J. Am. Chem. Soc. paper, that poly-L-Serine cannot be obtained by polymerizing L-Serine NCA. Rather, an intractable, branched polymer having few or no hydroxyl groups available for subsequent reaction is obtained. It was for this reason that a publication, mentioned in Reference 4 as being forthcoming and concerning the preparation of poly-L-Serine directly from L-Serine-NCA was not issued.



SPECTRUM NO. <u>5967</u>	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE <u>N 963</u>	_____	1. _____	_____
<u>L-SERINE</u>	PURITY <u>1 MG</u>	2. _____	_____
<u>PIERCE CHEM. CO.</u>	PHASE <u>PELLET, KBr</u>	DATE <u>11-19-69</u>	_____
<u># 37955</u>	THICKNESS _____	OPERATOR <u>W. LADROGA</u>	_____

SPECTRUM NO. 5967  
SAMPLE N963 L-SERINE

Figure A-4 INFRARED SPECTRUM OF L-SERINE

APPENDIX B

POLY-L-TYROSINE SOLUBILITY INVESTIGATION

## APPENDIX B

### POLY-L-TYROSINE SOLUBILITY INVESTIGATION

It had been learned from Dr. Ryan, Pilot Chemicals Corp., Waltham, Mass., (a manufacturer of poly-L-Tyrosine) that a basic solution, pH 10-11, is necessary to dissolve the polymer. Solution, he advised, is attained only with difficulty. He recommended effecting solution by suspending the polymer in water and adding alkali solution slowly with stirring. For this application, the presence of alkali metal salts were considered undesirable because they would be deposited upon evaporation and interfere with the bond to be formed subsequently with the polymer. Therefore, it was decided to substitute aqueous ammonia for solution because no residue would remain upon solvent evaporation. It was found that about 50 percent of the polymer would dissolve readily. The undissolved portion was filtered and the solution evaporated onto an aluminum coupon by infrared lamps. Some poly-L-Tyrosine was deposited, but there was attack of the aluminum surface by the ammonia solution. In an attempt to avoid this attack, the solution was heated to drive off excess ammonia before another deposition was attempted. Nevertheless, some attack was still evident. Therefore, it was decided to investigate the solubility of the polymer in organic solvents.

Methyl alcohol and pyridine were tried first. Little or no solubility was observed and these solvents were not considered further. Dimethylformamide (DMF) was tried next. This is a polar liquid known to be an excellent solvent for many polymers and additionally it does not attack aluminum. The poly-L-Tyrosine swelled almost immediately and soon, only a very small portion remained undissolved. This portion was brought into solution by heating. It was learned later that DMF had been used successfully as a solvent for casting films for infrared studies (Ref. 8).

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